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## The Crystal and Molecular Structure of 4-Methyl Sulfonic Acid (*p*-Toluenesulfonic Acid) Monohydrate, $C_7H_8SO_3 \cdot H_3O^+$ , an Oxonium Salt

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The crystal structure of *p*-toluenesulfonic acid monohydrate has been determined using 1274 three-dimensional intensities measured on a Picker four-circle diffractometer. The crystals are monoclinic, space group  $P2_1/c$ , with unit-cell dimensions  $a = 5.881$ ,  $b = 7.431$ ,  $c = 20.085$  Å, and  $\beta = 97.95^\circ$ . The structure was solved by the heavy-atom technique and refined by full-matrix least-squares to an  $R$  of 0.04. The structure consists of a pyramidal oxonium ion,  $H_3O^+$ , hydrogen bonded to three oxygen atoms of different sulfonate groups. These hydrogen bonds are fairly short, average 2.53 Å. The S...O bond distances are equal (average 1.456 Å) within experimental errors. The conformation of the sulfonate group is such that one of the S-O bonds is approximately normal to the ring. This is the preferred conformation for the sulfonate group. The conformation of the methyl group is such that two of its hydrogen atoms make projected angles of about  $60^\circ$  to the benzene plane while the third hydrogen atom is close to the plane.

#### Introduction

A survey (Sundaralingam, unpublished results) of the crystal structures of substituted benzenoid derivatives

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revealed that the benzenoid rings do not generally possess hexagonal symmetry with the exception of the fully substituted benzenoid derivatives, e.g.  $C_6Cl_6$ . The mode of distortion of the aromatic nucleus is dependent on the number of substituents, their relative positions on the ring and their electronic properties, i.e. whether they are electron withdrawing or electron releasing. In *para*-substituted derivatives, the aromatic ring possesses a mirror plane through C(1) and C(4)



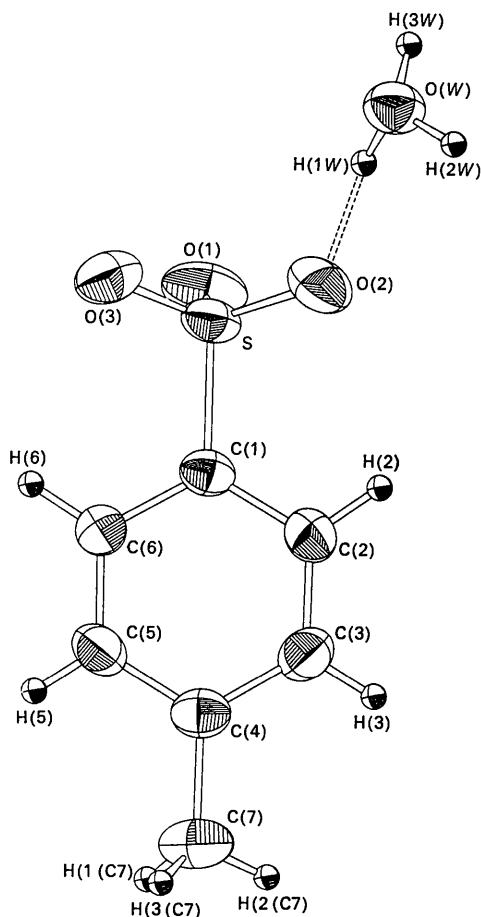


Fig. 1. Thermal ellipsoid plot of the non-hydrogen atoms.

$2\theta$  limit of  $133^\circ$  using  $\text{Cu K}\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation and the  $2\theta$  scan mode at a scan speed of  $2^\circ \cdot \text{minute}^{-1}$ . The crystal was mounted with the  $a$  axis coincident with the  $\varphi$  axis. Altogether 1505 independent reflections were collected and 1274 were considered to be nonzero using the criterion that a reflection is observable if  $I > 1.4\sigma(I)$ , where  $\sigma(I) = [C_i + (0.05 C_n)^2]^{1/2}$ , is the standard deviation in the intensity;  $C_i$  is the total number of scanned plus background counts, and  $C_n$  is the scanned minus background counts. A standard reflection was used to monitor the crystal stability and the fluctuation in the electronics. During the intensity measurements a maximum variation in the standard of 4.5% was observed. The data were corrected for the variation in the standard and the usual Lorentz and polarization factors, but no correction was made for absorption ( $\mu = 30.3 \text{ cm}^{-1}$ ).

### Structure determination and refinement

The structure was determined by the heavy-atom technique. The sulfur coordinates were obtained from the Harker sections of a Patterson map, and the rest of the atoms were located in the three-dimensional electron density map using sulfur phases. The initial  $R$  index on all non-hydrogen atoms was 0.29. Two cycles of least-squares isotropic refinement dropped the  $R$  value to 0.13 and two cycles of anisotropic refinement dropped the  $R$  to 0.077. At this stage a difference electron density map was calculated and all the hydrogen atoms were located including those of the water. An unexpected feature of the structure was that the water molecule was in the protonated form

Table 3. Final positional and thermal parameters of *p*-toluenesulfonic acid

Estimated standard deviations are given in parentheses.

The temperature factor ( $\times 10^4$ ) for non-hydrogen atoms is of the form

$$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + \beta_{23}kl)].$$

The hydrogen atoms were given the thermal parameters of the atoms to which they were attached.

	$x/a$	$y/b$	$z/c$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{33}$
S	0.3037 (1)	0.1442 (1)	0.10646 (3)	266 (2)	210 (2)	16 (9)	-39 (1)	17 (1)	-14 (0)
O(1)	0.1931 (4)	-0.0246 (3)	0.08392 (10)	582 (9)	247 (5)	26 (1)	-105 (6)	33 (2)	-36 (1)
O(2)	0.5452 (3)	0.1480 (4)	0.09892 (10)	290 (7)	440 (7)	27 (1)	-0 (6)	37 (2)	-6 (2)
O(3)	0.1774 (3)	0.2973 (3)	0.07465 (8)	349 (7)	256 (5)	20 (0)	-60 (4)	-1 (1)	4 (1)
O(W)	0.7830 (4)	0.2488 (3)	0.00965 (10)	312 (7)	218 (4)	21 (1)	-23 (5)	12 (1)	-12 (1)
C(1)	0.2891 (4)	0.1583 (3)	0.19290 (11)	260 (7)	144 (5)	17 (1)	-22 (5)	12 (1)	-9 (1)
C(2)	0.4678 (5)	0.0932 (4)	0.23843 (13)	269 (9)	183 (6)	23 (1)	34 (6)	14 (2)	-8 (2)
C(3)	0.4502 (5)	0.0982 (4)	0.30599 (13)	334 (9)	178 (6)	21 (1)	42 (6)	-3 (2)	1 (1)
C(4)	0.2579 (5)	0.1679 (3)	0.32941 (12)	319 (9)	141 (5)	19 (1)	-22 (5)	14 (2)	-3 (1)
C(5)	0.0822 (5)	0.2316 (4)	0.28305 (13)	271 (9)	192 (6)	23 (1)	16 (6)	27 (2)	-8 (2)
C(6)	0.0949 (5)	0.2288 (4)	0.21507 (12)	234 (8)	196 (6)	19 (1)	16 (1)	5 (2)	-5 (1)
C(7)	0.2398 (7)	0.1739 (5)	0.40364 (14)	519 (14)	241 (8)	20 (1)	-14 (8)	22 (2)	-0 (2)
H(2)	0.5989 (44)	0.0528 (34)	0.2182 (12)						
H(3)	0.5634 (46)	0.0478 (36)	0.3368 (13)						
H(5)	-0.0357 (45)	0.2777 (35)	0.3004 (13)						
H(6)	-0.0256 (41)	0.2721 (32)	0.1821 (12)						
H(1 C7)	0.0821 (50)	0.0936 (39)	0.4161 (13)						
H(2 C7)	0.3466 (52)	0.1020 (41)	0.4291 (14)						
H(3 C7)	0.2319 (50)	0.2984 (42)	0.4255 (14)						
H(1 W)	0.6852 (50)	0.2043 (36)	0.0362 (14)						
H(2 W)	0.9140 (56)	0.2597 (36)	0.0373 (14)						
H(3 W)	0.7757 (44)	0.1715 (37)	-0.0264 (14)						

(oxonium ion  $\text{H}_3\text{O}^+$ ), the three hydrogen atoms being attached to the water oxygen atom at geometrically plausible positions. This was confirmed when no hydrogen atom at covalent bonding distance to any of the sulfonate oxygen atoms was found, and the three S-O bond distances were nearly equal. Further least-squares refinement varying the hydrogen positional coordinates, but keeping their temperature factors fixed at the average isotropic values of the heavy atoms to which they are covalently bound, lowered the *R* index to the final value of 0.04 for the 1274 observed reflections. The refinement was terminated at this point since the ratios of the shifts to estimated standard deviations in the parameters were all considerably less than 0.1. The weighting scheme employed in the least-squares refinement was  $1/\sqrt{W} = \sigma(F) + 0.05|F|$ , where  $\sigma(F) = \{[C_t + (0.05C_n)^2]C_n\}^{1/2}/2(Lp)^{1/2}$ . The scattering factors used throughout this work were those of Hoerni & Ibers (1954) for carbon and oxygen, Cromer & Waber (1965) for sulfur, and Stewart, Davidson & Simpson (1965) for hydrogen.

The observed and calculated structure factors are listed in Table 2. The atomic parameters and their estimated standard deviations are given in Table 3. The anisotropic vibrations of the non-hydrogen atoms are represented by the thermal ellipsoid drawing (Johnson, 1965) in Fig. 1.

The full-matrix least-squares program used in this work is that of Busing, Martin & Levy (1962) modified for the Univac 1108 computer in these laboratories

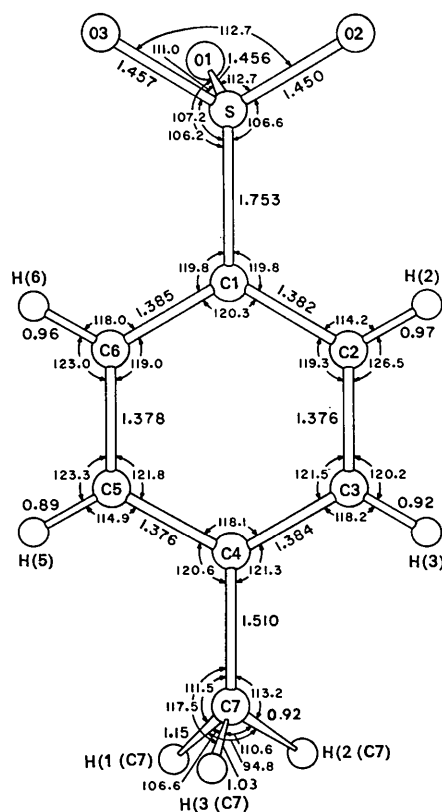


Fig. 2. Bond lengths and angles.

Table 4. *The geometry of the sulfonate group*

C-S and O-S bond distances and C-S-O and O-S-O bond angles in *p*-toluenesulfonic acid and related compounds.

Compound	C-S	O-S	C-S-O	O-S-O	Reference
<i>p</i> -Toluenesulfonic acid monohydrate	1.752 (2) Å	1.456 (2) Å	106.2 (0.1)°	112.7 (0.1)°	Present work
		1.450	106.6	111.0	
		1.457	107.2	112.7	
		1.456	106.2	107.2	
1,5- <i>endo</i> -Methylenequinolizidinium <i>p</i> -toluenesulfonate	1.780 (4)	1.461 (4)	105.4 (0.2)	111.6 (0.2)	Huber (1969)
		1.456	105.7	113.9	
		1.455	105.5	113.7	
		1.455	105.5	113.7	
2-Diazonium 4-phenolsulfonate monohydrate	1.76 (1)	1.46 (1)	104 (0.5)	113 (0.5)	Greenberg & Okaya (1969)
		1.46	107	114	
		1.44	106	112	
		1.44	106	112	
Ammonium <i>o</i> -carboxybenzenesulfonate	1.775 (4)	1.444 (4)	106.9 (0.2)	112.3 (0.2)	Okaya (1967)
		1.436	105.9	111.0	
		1.453	106.3	113.9	
		1.453	106.3	113.9	
Sulfanilic acid monohydrate	1.77 (2)	1.42 (2)	107 (2)	110 (2)	Rae & Maslen (1962)
		1.46 (2)	106 (2)	112	
		1.44 (2)	105 (2)	116	
		1.44	105	116	
2- <i>p</i> -Toluidinyl 6-naphthalenesulfonate*	1.770 (2)	1.452 (1)	106.1 (0.1)	110.5 (0.1)	Cameran & Jensen (1969)
		1.453	106.1	113.0	
		1.440	105.8	114.3	
		1.434 (4)	108.7	111.2 (0.2)	
Sulfuric acid monohydrate	—	1.462	103.1	112.4	Taesler & Olovsson (1968)
		1.449	107.8	113.0	
		1.560 (S-OH)			
		1.436-1.461	105.4-107.2	110.5-114.3	
		1.451	106.1	112.6	
		1.451	106.1	112.6	

\* This is the only naphthalene derivative, the rest are benzene derivatives.

† The compounds 2-diazonium 4-phenolsulfonate monohydrate, sulfanilic acid monohydrate and sulfuric acid monohydrate were omitted in the ranges and averages because the former two have high e.s.d.'s while the latter is not a sulfonate. They are given here only for comparison.

(Rao, 1968). The Fourier programs and other miscellaneous programs used in this work were those of Rao (1968).

### Results and discussion

The bond lengths and bond angles are shown in Fig. 2. The average estimated standard deviations in bond distances are: S–O, 0.002; C–S, 0.002; C–C, 0.003 Å; and C–H=O–H, 0.03 Å; in bond angles: O–S–O, 0.1; O–S–C, 0.1; S–C–C, 0.2; C–C–C, 0.2; C–C–H, 1.1; H–C–H=H–O–H, 1.4°.

The exocyclic C(4)–C(7) bond length of  $1.510 \pm 0.004$  Å, does not differ significantly from the accepted value of  $1.501 \pm 0.004$  Å (Lide, 1962) for a  $Csp^2$ – $Csp^3$  single bond. The average aromatic C–C bond distance is 1.380 Å which is marginally shorter than the accepted value of  $1.394 \pm 0.005$  Å (Sutton, 1965). There is an approximate plane of symmetry through C(1) and C(4). The central bonds C(2)–C(3) and C(5)–C(6) average 1.377 Å, while the remaining ring bonds average 1.382 Å. Although not pronounced, there is a small tendency for the central C–C bonds of *para* substituted benzene derivatives to be shorter than the remaining

ring bonds (Huber, 1969). The effect can be explained by the resonance theory. It might also be pointed out that the internal valence angles (range 118–122°) at the substituted carbon atoms generally show significant departure from the ideal trigonal value of 120°.

The S–C and average S–O bond lengths are  $1.753 \pm 0.002$  and  $1.454 \pm 0.003$  Å respectively. They are generally in good agreement with those observed in similar structures (Table 4), average C–S, 1.769 Å and average O–S, 1.451 Å. The variations in these distances are attributed to differences in conformation of the sulfonate group and the number and nature of the groups to which the sulfonate group is hydrogen bonded.

The similarity in the three S–O bonds,  $1.456 \pm 0.002$ ,  $1.450 \pm 0.002$ ,  $1.457 \pm 0.002$  Å, demonstrates that there is no hydrogen atom attached to any of the oxygen atoms; the presence of a covalently bound hydrogen atom on the oxygen atom is expected to increase the S–O(H) bond distance by about 0.1 Å as seen in sulfuric acid monohydrate (Taesler & Olovsson, 1968), Table 4. Furthermore, the difference Fourier synthesis revealed that the acid proton was attached to the water molecule, yielding an oxonium ion.

There is marked difference, about 5.5°, between the C–S–O (average 106.7°) and O–S–O angles (average 112.2°). Greenberg & Okaya (1969) have pointed out that this is a general property of the sulfonate group. It may be noted that the O–S–OH and O–S–O bond angles in sulfuric acid monohydrate are extremely similar to the O–S–C and O–S–O angles respectively of the sulfonates.

### Planarity of ring and molecular conformation

The benzene ring is planar within the errors of determination, Table 5; the substituent methyl carbon atom lies in this plane, but the substituent sulfur atom is markedly displaced (0.07 Å) from the ring plane. However, in Huber's (1969) compound the benzene ring was found to show small but significant distortion from planarity, indicating that even the aromatic ring can be subjected to distortions by the crystal packing forces.

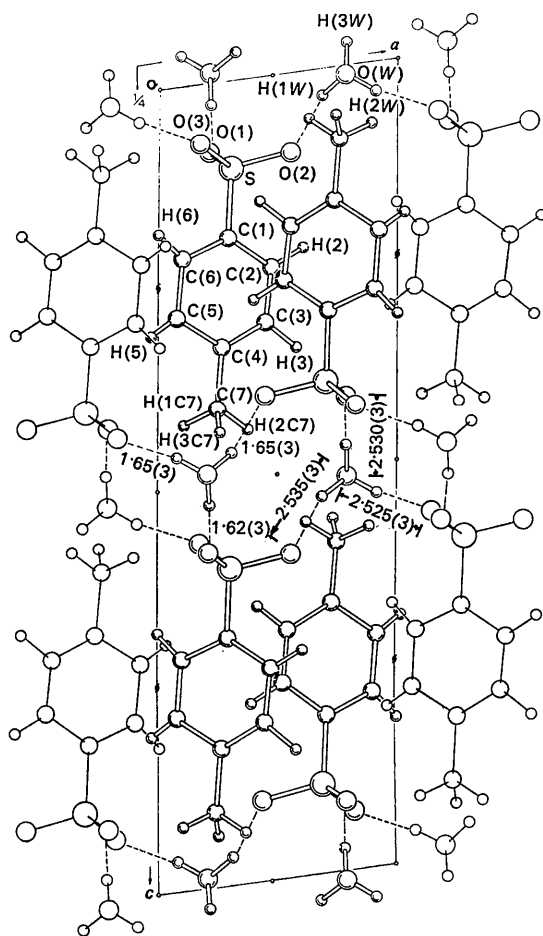


Fig. 3. Hydrogen bonds.

Table 5. The least-squares plane

Atoms included in plane	$\Delta$	Atoms not included in plane	$\Delta$
C(1)	0.001 Å	S	0.070 Å
C(2)	-0.001	C(7)	-0.007
C(3)	0.001	H(2)	-0.05
C(4)	-0.002	H(3)	0.06
C(5)	0.003	H(5)	-0.02
C(6)	0.002	H(6)	0.00
r.m.s. $\Delta$	0.002 Å		

The direction cosines of the plane relative to the a, b, c\* directions are -0.415, -0.908 and -0.063; the origin-to-plane distance is -1.795 Å.

Table 6. *Conformation of the sulfonate and methyl groups*

Sulphonate group		Methyl group	
O(1)–S–C(1)–C(2)	92.2°	C(3)–C(4)–C(7)–H(1 7)	–121
O(1)–S–C(1)–C(6)	–85.2	C(5)–C(4)–C(7)–H(1 7)	59
O(2)–S–C(1)–C(2)	–28.2	C(3)–C(4)–C(7)–H(2 7)	–15
O(2)–S–C(1)–C(6)	154.1	C(5)–C(4)–C(7)–H(2 7)	165
O(3)–S–C(1)–C(2)	–149.2	C(3)–C(4)–C(7)–H(3 7)	116
O(3)–S–C(1)–C(6)	33.2	C(5)–C(4)–C(7)–H(3 7)	–64

Table 7. *Hydrogen bond distances and bond angles*

O(1)...O(W)	2.530 Å	S — O(1) ... O(W)	113.6°
O(1)...H(3W)	1.62	S — O(1) ... H(3W)	136
O(2)...O(W)	2.535	S — O(2) ... O(W)	136.4
O(2)...H(1W)	1.65	S — O(2) ... H(1W)	133
O(3)...O(W)	2.525	S — O(3) ... O(W)	119.4
O(3)...H(2W)	1.65	S — O(3) ... H(2W)	117
		O(1)...O(W)...O(3)	109.7
		O(2)...O(W)...O(1)	115.1
		O(2)...O(W)...O(3)	103.5

The torsional angles about the C(1)–S bond and the C(7)–C(4) bonds are shown in Table 6. The S–O(1) bond is approximately normal to the ring while the S–O(2) and S–O(3) bonds make angles of about –28 and 33° respectively to the benzene bonds closest to them. Similar conformations are observed for the sulfonate groups in the related compounds.

The conformation of the methyl group is such that one of the methyl hydrogen atoms makes a torsional angle of 15° to the plane of the aromatic ring, while the remaining hydrogen atoms make angles close to 60° to the plane. In Huber's (1969) compound one of the methyl hydrogen atoms is approximately normal to the ring plane. Thus, crystal packing forces influence the conformation of the methyl group.

#### Geometry of the oxonium ion and hydrogen bonding

The oxonium ion exhibits a pyramidal configuration; H(1W)–O(W)–H(2W), 103°, H(2W)–O(W)–H(3W), 119° and H(1W)–O(W)–H(3W), 106°. The hydrogen bond distances and angles involving the oxonium ion are shown in Table 7.

The sulfonate oxygen atoms accept one hydrogen bond each from three different oxonium ions, the O(W)–H...O distances are 2.525 ± 0.003, 2.530 ± 0.002 and 2.535 ± 0.003 Å, Fig. 3. These distances are shorter than the normal O–H...O hydrogen bonds indicating that the O<sup>+</sup>–H...O<sup>δ-</sup> hydrogen bonds are stronger than those between neutral oxygen atoms. Similar but slightly longer hydrogen bonds were observed in sulfuric acid monohydrate, HSO<sub>4</sub><sup>-</sup>·H<sub>3</sub>O<sup>+</sup> (Taesler & Olovsson, 1968). However, the hydrogen bonds involving the *p*-toluenesulfonate moiety in the complex with 1,5-*endo*methylenequinolizidine (Huber,

1969) are considerably longer. Therefore, the short hydrogen bonds are probably characteristic of the sulfonate anion and the oxonium cation.

The molecules are packed in a herring bone fashion, a characteristic manifestation of homoaromatic compounds. The intermolecular contacts are all greater than the van der Waals distances.

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